

ICASE REPORT

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VALUE METHOD TO THE CALCULATION OF BORN-OPPENHEIMER
VIBRATIONAL EIGENENERGIES FOR THE DOUBLE MINIMUM
E, F $1\Sigma_g^+$ STATE OF THE HYDROGEN MOLECULE"

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A NOTE ON "THE APPLICATION OF THE FINITE-DIFFERENCE BOUNDARY
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ABSTRACT

This note is to comment upon aspects of the title subject for the case where an interatomic potential is defined at only a finite number of imprecise data points. Discussion topics include numerical interpolation, physical extension of the region of definition, and Richardson extrapolation of vibrational wavefunction expectation values.

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Two very important aspects of application of the finite-difference boundary-value method [1],[2],[3] (FDBVM) to vibrational eigenproblems of diatomics

$$\left[-\frac{1}{2\mu} \frac{d^2}{dR^2} + U(R) \right] f_v(R) = E_v f_v(R) \quad (1)$$

for which the potential $U(R)$ is defined at only N data points distributed over a limited domain $R_1 \leq R \leq R_N$ are addressed by Truhlar and Tarara (TT) in a recent paper [4]. These are (a) the effect of using extensions to $U(R)$ for regions outside of the domain and (b) the continuous representation of $u_i = U(R_i)$ on the domain. We agree as to their importance but find the actual procedures used by TT to be subject to critical comment both from a physical and a numerical point of view.

To obtain a physically meaningful solution of (1), if derived eigenfunctions are to describe tunnelling into the regions beyond the given domain, requires extension of $U(R)$ because in the FDBVM the eigenfunction is zero within $h(=R_{i+1}-R_i)$ of the extremes of the domain over which U is defined. Using the $E, F \sum_g^+$ potential curve data of Kolos and Wolniewicz (KW)[5], TT demonstrated that fitting an extension to $U(R)$ for the region $.5 \leq R \leq R_1 = 1.0$ has considerable effect on even the lowest energy level. We feel that the function chosen by TT to extend $U(R)$ is poorly conceived because it assumes an incorrect asymptotic behavior as $R \rightarrow 0$. The true $U(R)$ should go as $R^{-1} + g(R)$ where $g(R)$ is everywhere bounded. Thus R_i^{-1} should first be subtracted from u_i and the resulting values should be fitted by use of a bounded functional form such as

$$g(R) = \left(\sum_{k=0}^m a_k R^k \right)^{-1}, \quad a_0 \neq 0. \quad (2)$$

Then $U(R) = R^{-1} + g(R)$ for $R < R_1$ and hence $U(R) - R^{-1} - g(R)$ goes to zero as R goes to R_1 from the positive side. In addition to the adjusted Davidson point [4],[6] ($R = .5$), one may also make use of the helium 2^1S (1s2s) united atom energy, $g(0)$. We suggest using more of the KW points, say up to $R = 1.9$, and fitting $g(R_i)$ by least-squares, giving heavy weight to $g(1.0)$ in order to maintain continuity. It is desirable to use the derivative at $R = 1.0$ to improve the fitting but for the general case one cannot count on having derivative values.

To obtain a continuous representation for the potential curve, TT follow an earlier suggestion [7], i.e., interpolation of the products, p_i , of an analytic function, $\alpha(R)$, and the data points, u_i . Such a procedure is questionable because numerically the values of the product points must be maintained to more significant figures than the original data points in order that $p_i/\alpha(R)$ will restore u_i exactly. The implication is that interpolation of p_i must be of higher order accuracy than that of u_i . A better procedure would be to subtract from the u_i an appropriate $\alpha(R)$ which is sufficiently close to $U(R)$ so that the differences, $u_i - \alpha(R_i)$, which are to be interpolated, would have fewer significant figures than u_i . We suggest that interpolation of $u_i - R^{-1} - g(R)$ for $R_1 \leq R \leq R_N$ is very appropriate.

TT have employed Lagrange interpolation, a procedure which is known to fail in certain situations [8]. There is quite a large literature now describing cubic spline methods [8],[9] which are fourth order accurate and yield a continuous, smoothed interpolant (continuous first and second derivatives). It is a considerable oversight not to have mentioned these methods. Furthermore, as implied by TT, interpolation in a strict sense is not appropriate in this problem because the data points are actually inaccurate at least to the tune of roundoff error. Hence, it is more correct to use a method which takes any known

error in the data points into account. Such a method, based on cubic splines is described by Reinsch [10], [11] who has given a code which when used does not require one to drop data points, a somewhat arbitrary practice. We note that relative to the dissociation limit of 0.625 hartree, the data points are given to just six figures, thereby imposing a practical mathematical limit on the accuracy of derived dissociation energies of vibrational states.

There also appears to be a severe misconception regarding Richardson extrapolation [12], [2] of the expectation values of certain operators. Richardson extrapolation is effective only when the coefficients which multiply successive powers of h^2 in the approximation to a given quantity are entirely independent of h . The eigenvalues and expectation values of operators which commute with the hamiltonian are such quantities as are the values of the eigenfunctions, $h^{-1}f_v(R_i)$, at FD grid points. The latter values may be extrapolated to higher order only at the common points of successive FD approximations to $f_v(R)$. To extrapolate $h^{-1}f_v(R_i)$ effectively then, the different grids employed ought to have many points in common. This implies that the best choice for successive grids is to halve the interval length. To obtain expectation values to a high order accuracy one may first extrapolate $f_v(R_i)$ to the desired level (on the coarsest grid) and then evaluate the expectation value integral. Since the function is known only pointwise, the FD approximation to it must be regarded as a quadrature formula. Each quadrature rule has its own characteristic order of accuracy and so a quadrature rule must be chosen which has an accuracy equal to or higher than the accuracy of $f_v(R)$. An alternate and operationally simpler way to improve the expectation values is to extrapolate them instead of the $h^{-1}f_v(R_i)$. This cannot be accomplished by using quadratures over different grids since then the coefficients which multiply successive powers of h^2 in the error term would

depend on h . The only recourse is to again use a higher order quadrature formula, keeping the quadrature points fixed. In order to improve the accuracy of the expectation values, the quadrature formula can be successively evaluated using values of $f_v(R_i)$ at the quadrature points obtained from FD computations over different grids. Both methods to improve the accuracy of expectation values by Richardson extrapolation share two properties. First, the error cannot be reduced beyond that of the quadrature formula. Second, the extrapolation process will be effective only when the successive FD calculations employ a large number of common points. Since TT used grids of $1/50$, $1/60$, and $1/70$ (which have relatively few points in common), we infer that they have not recognized the limitations of Richardson extrapolation and that their results for the expectation value of R^{-2} are consequently only of order h^2 accurate.

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